

1 489 084

- (21) Application No. 46858/74 (22) Filed 29 Oct. 1974
(23) Complete Specification filed 28 Oct. 1975
(44) Complete Specification published 19 Oct. 1977
(51) INT. CL.⁸ B41M 3/10
(52) Index at acceptance
B6A 26X7 42A
B6C A25 A26

(72) Inventors JACQUES EHRETSMANN
ALAIN ROMAN
PIERRE CHEVREUX
MANFRED WUST
JOHN DAVID BARNARD



(54) SIMULATED WATERMARKING

(71) We, TULLIS RUSSELL & COMPANY LIMITED, a British company, of Markinch, Glenrothes, Fife, KY7 6PB, Scotland, do hereby declare the invention, for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:—

The traditional methods of forming watermarks in a paper sheet consist in forming the sheet on a suitably profiled mould of a cylinder mould paper machine, or by applying a suitably profiled dandy roll to the wet sheet on the forming table of a Fourdrinier machine. Both methods cause a differential distribution of the paper making fibres in the area of the watermark resulting in a variation in the translucency of the paper. However, suitably profiled moulds and dandy rolls are very expensive, and with the high productive capacity of modern paper making machines, it is not practical or economic to manufacture comparatively small quantities of paper with select watermarks. Furthermore, the localised disruption of the surface of the paper in the area of the mark, often leads to difficulties in the printing of characters intended for use in automatic data processing systems such as optical or magnetic character recognition systems, which may lead to misreading when documents printed with such characters are processed with consequent disruption to the system.

To meet this problem there have been a number of proposals for the formation in a paper sheet of simulated, so called "chemical", watermarks. These simulated watermarks are generally formed by impregnating the finished paper with a resin in the area of the desired watermark to increase the translucency of the paper over that area.

In one typical proposal the paper is impregnated with a solution of a curable

synthetic resin composition in an organic solvent after which the organic solvent is evaporated off and the resin composition is allowed to cure in situ. This proposal has the disadvantage that the process is slow, even amounting to some days while the resin composition cures, and the definition of the resulting simulated watermark is poor owing to the migration of the resin composition solution along the paper fibres after impregnation and before the organic solvent has been evaporated off. Furthermore one potentially important use for simulated watermarks is in the field of security papers and the process is not acceptable for use on sensitised security paper owing to the likelihood of the solvent action or chemical action of various components of the resin composition initiating the colour or other security reaction in the paper.

In accordance with the present invention, in a method of producing a simulated watermark in a paper sheet, the sheet is impregnated in the desired watermark pattern by a transparentising composition, which is itself fluent, and which is polymerisable upon being activated by radiation to yield an insoluble resin matrix having a refractive index approximating to that of the paper, and the composition is cured in situ by irradiating the sheet with activating radiation.

As with known chemical watermarks, the composition is generally applied to the finished paper.

In a polymerisable composition of the kind utilised in the method according to the invention, the radiation which initiates the polymerisation acts by raising the energy level of the molecules of a radiation sensitive component of the polymerisable composition almost instantaneously to a higher energy level excited state from which free radicals are generated in sufficient concentration to cause polymerisation to take place

in under one minute and preferably, under suitable conditions, in under one second.

It is this speed of curing of the transparentising composition in situ which leads to the most significant advantages of the invention. It is not necessary to store large quantities of paper under treatment while the curing takes place. There is little danger of the fluent composition migrating along the paper fibres to blur the definition of the watermark prior to being solidified in the paper upon curing. The clarity and definition of the mark are thus high and it is thus possible to apply the watermark and subsequent printing operations in one pass on a suitably adapted multi-station printing press. For example, on a multi-colour press, the first station could be adapted for watermarking, with a radiation drier attached, with conventional printing operations taking place at the second and subsequent stations. This would have obvious economic advantages and could be used in printing commercial stationary, prestige stationary as well as security documents and cheques. Furthermore, the method is particularly useful for applying a simulated watermark to sensitised security papers as the fluent transparentising composition is fluent, that is liquid or pasty, for too short a time in the paper to initiate significantly any security reaction, and the avoidance of the need for an appreciable quantity of organic solvent precludes any security reaction being initiated prematurely by the solvent. Also, it is possible to apply the watermark accurately to register so that the mark can be located in the same position on successive sheets. This is not possible with conventional mould or dandy marks, because of the variable shrinkage which occurs during the drying of the paper web.

The actual form of the activating radiation is not critical and it may consist of electromagnetic radiation such as ultra violet radiation, x-radiation or gamma-radiation; or particle radiation such as alpha-radiation, beta-radiation, or high energy beams of protons or neutrons. The only stipulation is that the polymerisable transparentising composition should be responsive to industrially available doses of the radiation to an extent sufficient to initiate the polymerisation. Taking all things into consideration, it is preferred to use ultra violet radiation and a photopolymerisable transparentising composition which responds to ultra violet radiation.

In order for the applied composition to act as a transparentising composition it has to provide, where it is applied, an area of increased translucency and this necessitates that the cured polymer should have a refractive index approximating that of paper since the transparentising effect deteriorates with

increasing difference between the refractive index of the paper and cured composition. In practice, since papers generally have a refractive index between 1.4 and 1.7, the polymerisable transparentising composition will therefore be one that forms, upon curing, a solid transparent insoluble colourless material having an appropriate refractive index between 1.4 and 1.7.

The composition normally comprises a polymerisable unsaturated monomer and a polymerisable unsaturated prepolymer and a polymerisation initiator that will be stimulated by the chosen radiation, and since it does of course have to form an insoluble product it is preferred that at least one of the components of the composition is polyunsaturated, in practice polyethylenically unsaturated.

A suitable polymerisable transparentising composition comprises one or more unsaturated monomers, consisting of an acrylic, methacrylic, vinyl or allylic composition and one or more unsaturated prepolymers, together with one or more radiation-stimulated polymerisation initiators. A particular advantage of using both an unsaturated monomer and an unsaturated prepolymer is that the monomer may act as a solvent for the prepolymer during impregnation, without the need for any additional solvent to be evaporated off subsequently. Furthermore, upon curing, there will be extensive grafting and/or cross-linking of the prepolymer chains by the monomer resulting in a three dimensional resin matrix which is virtually impossible to remove from the paper.

As a monomer one can utilise, for example, vinyllic compounds such as styrene, vinyl toluene, divinyl benzene, *p*-methyl styrene, acrylic acid, methacrylic acid, acrylic or methacrylic acid esters, particularly the mono or more preferably the di-, tri- or polyacrylic or methacrylic esters of a di- or polyhydric alcohol such as ethylene glycol, di-, tri- or polyethylene glycol, propylene glycol, 1,3 butane diol, 1,4 butane diol, 1,6 hexane diol, neopentyl glycol, trimethylol propane and pentaerythritol; dimethylaminoethyl methacrylate, glycidyl acrylate or methacrylate, unsaturated amides such as acrylamide, methacrylamide, *N,N'*-methylenebis-acrylamide or *N,N'*-hexamethylenebisacrylamide; or allylic compounds such as the *N*-allylacrylamide, ethylenebisallylmalate, diallylmalate, triallylcyanurate and diallylmalamine.

As prepolymer one can use, for example, an unsaturated polyester that is to say the ester produced from a polyhydric alcohol and a polycarboxylic acid or anhydride, of which at least one contains a double bond. For example one can use an unsaturated polyester produced from ethylene glycol or

propylene glycol with maleic anhydride or fumaric acid. One polyester resin which is found to give fast curing is sold by the Resinous Chemicals Division of Berger Chemicals under the name Alpolit (Registered Trade Mark) VUP 31181.

Other types of resins which may be used include acrylated epoxy resins e.g. the reaction product of acrylic acid with a bisphenol A-epichlorohydrin resin; isocyanate adducts obtained by reacting a hydroxy alkyl acrylate ester with a polymer containing isocyanate groups; and epoxy oil acrylates obtained by reacting e.g. acrylic acid with epoxidised soya bean oil.

The polymerisable composition may also include a polymer which reacts with the monomer and/or prepolymer during the irradiation-curing, and which may be, for example a plasticiser for improving the shrinkage characteristics of the final polymerisation product. A suitable polymer is that sold by Mitchell and Smith under the name "Polymaster (Registered Trade Mark) 2460".

Where the radiation to be used is ultra violet radiation, the photo-initiator may be aryl sulphonyl chlorides such as naphthalene-2-sulphonyl chloride and toluene-4-sulphonyl chloride; an aromatic carbonyl compound such as benzoin, or a benzoin derivative, particularly a benzoin alkyl ether such as benzoin methyl ether, or benzoin n-butyl ether; acetophenone, or derivatives of acetophenone such as diethoxy-acetophenone; benzophenone, or derivatives of benzophenone such as 3, 3', 4, 4' benzophenone tetracarboxylic acid dianhydride; anthraquinone, or derivatives of anthraquinone, particularly 2-substituted alkyl and halogen derivatives such as 2-methyl anthraquinone, 2-t-butyl anthraquinone, and 2-chloro anthraquinone; and xanthone, or derivatives of xanthone such as thioxanthone, or 2-chloro thioxanthone.

In many cases it is advantageous to use a combination of two of the above initiators as this gives faster curing than either of the initiators alone at the equivalent concentrations.

In some cases it is also advantageous to use an amine in conjunction with an aromatic carbonyl compound, to enhance the speed of curing. It is well known that the use of amines, particularly tertiary alkyl amines can enhance the speed of curing with aromatic carbonyl compounds, and the mechanism is generally believed to be via a charge transfer complex formed between the excited state of the carbonyl compound and the amine. Suitable amines are triethylamine, triethanolamine and N, N dimethyl ethanolamine.

One can use any appropriate process for impregnating the paper with the trans-

parentising composition in the selected area. A printing process is simplest however and gravure or continuous screen printing are preferred. For gravure printing, the polymerisable transparentising composition preferably has a viscosity between 10 and 1000 cP, preferable between 20 and 700 cP. For screen printing, the composition preferably has a viscosity of between 100 and 3000 cP, preferable between 300 and 2000 cP.

In order to assist the penetration of the polymerisable transparentising composition into the paper before irradiation, we find that it is advantageous to apply suction to the face of the paper opposite to that to which the composition is applied. The actual amount of suction depends upon the required depth of penetration of the composition into the paper, the porosity of the paper and the viscosity of the resin. However in general the suction will amount to a few centimetres of mercury, for example a sub-atmospheric pressure of between 2 and 50 centimetres of mercury. The suction may be applied during the application of the composition to the paper or immediately afterwards.

The suction has the beneficial effects of speeding up the impregnation of the paper, improving the symmetry of the impregnation through the thickness of the paper, and improving the definition of the water mark by inhibiting any tendency of the composition to migrate laterally in the plane of the paper.

If the applied transparentising composition does not fully penetrate the paper and some of the composition remains and is subsequently cured on the surface of the paper, a surface gloss, which is detrimental to subsequent print receptability, may be formed in the area of the watermark. This difficulty can be overcome by treating the surface of the paper, at least in the area of the simulated watermark, after impregnation with the transparentising composition but before curing of the composition, with a small quantity of a solvent or diluent for the composition. The solvent or diluent may be applied in a fine spray or by means of a damping roller or pad.

It appears that the effect of the solvent or diluent application is to reduce the viscosity of the polymerisable composition at the surface of the sheet sufficiently to cause it to migrate into the body of the paper. However the quantity of the solvent or diluent used is so small that it does not lead to any of the disadvantages of the previous processes in which the transparentising composition is dissolved in an organic solvent for impregnation of the paper. The solvent or diluent will usually be readily volatile and will quickly evaporate off in the atmosphere, and par-

particularly upon irradiation of the paper, before the solvent has had time to initiate any security reaction.

The solvent or diluent which is applied to the surface of the paper may be, for example, one or more of the monomers previously mentioned; and alcohol such as methanol or ethanol; a ketone such as acetone or methyl ethyl ketone; an ester such as ethylacetate or butylacetate; a chlorinated solvent such as trichloroethylene, tetrachloroethane, or carbontetrachloride; or an aromatic hydrocarbon such as benzene or toluene.

This treatment eliminates any unwanted gloss on the surface of the paper in the area of a watermark and leaves the surface of the paper with its original qualities for printing.

One can subject the paper which has been impregnated with the transparentising composition, to the irradiation in any appropriate manner. For example the irradiation may be carried out with or without relative movement between the paper sheet and the source or sources of radiation. Also the radiation may be carried out at one time or in successive periods, for example to avoid overheating the paper during the irradiation.

In a process for producing a simulated watermark utilising the various optional and beneficial features described above, the treatment would be carried out in the following order:

1. Printing of the polymerisable transparentising composition onto the surface of the paper sheet.
2. Impregnation of the paper by the transparentising composition. This will commence upon the composition being printed on the paper and will proceed at a speed depending upon the porosity of the paper and the viscosity of the composition.
3. Suction is applied to the opposite surface of the sheet to draw the composition into the sheet. The suction may be applied during the printing or afterwards.
4. Light treatment of the printed surface with a solvent or diluent for deglossing.
5. Irradiation of the paper with the activating radiation to cure the transparentising composition in situ.

The excellent definition which is achieved in the simulated watermarks produced in accordance with the invention leads to the novel possibility of producing, particularly in security paper a simulated watermark pattern to give a Moiré effect. This is an optical effect wherein two or more geometric patterns, of say dots or lines, combine to form a further different geometric pattern. Good definition is required as the best effects are produced if the individual geometric patterns consist of very fine

closely spaced but discrete dots or lines.

In order to produce such an effect in a simulated watermark the transparentising composition may be printed on the paper sheet in the various patterns either in sequence or simultaneously.

The simulated watermark produced in accordance with the invention may have a colour tint by incorporating an appropriate colouring material in the transparentising composition. Two or more colours may be used to form a pictorial or other design and some of the differently coloured areas may overlap to produce other colours. However an additional security feature may be incorporated if the transparentising composition includes a colour former which only produces a colouration when subjected to a particular reaction.

The colouration may be produced by any conventional colour forming reaction such as the colouration of a colour former by the action of an acid or base, for example phenolphthalein and a base; or by an oxidation or reduction reaction; or by the formation of a complex between an organic compound and a metal ion. The colour forming compound may be formed in situ by a photochemical reaction occurring simultaneously with the photopolymerisation of the resin.

Alternatively the simulated watermark may contain an inhibiting reagent which prevents a colour forming reaction which could otherwise occur if it were not present. For example, the base paper may contain colour forming compounds which are inhibited in the area of the mark so that when subjected to the security reaction, the mark remains uncoloured, but the surrounding paper becomes coloured.

The colour forming reagents may be provided one in the watermark and the other by application to the paper surface when carrying out the security reaction. Alternatively, both the colour forming reagents are incorporated in powder or capsule form in the resin which forms the simulated watermark, the reagents being brought together for the colour formation upon application of pressure, such as by application of a stamp to the paper.

The security aspect and difficulty of falsification may be extended if there are two or more separately applied simulated watermarks which provide different colour forming effects. The parts which provide different colour forming effects may overlap to provide a combined watermark pattern.

Some examples of the production of a simulated watermark in accordance with the invention will now be described:—

Example 1

A photopolymerisable transparentising composition was prepared from 24% by

weight of styrene, 75% by weight of a commercial mixture consisting of 31% by weight of styrene and 69% by weight of an unsaturated polyester, and 1% by weight of naphthalene sulphochloride as a photoinitiator. The composition has a viscosity of 170 cP at 22°C. The styrene/polyester mixture had a viscosity of between 13 and 17 P at 25°C, and acid index of from 28 to 32, a refractive index of 1.540 at 20°C, a specific gravity of 1.14 at 20°C, an exothermic peak at 280°C and a gelling time (test SPI, TM18) of five minutes, and was produced under the mark "SYNOLITE (Registered Trade Mark) 375" by the Synres Company.

The composition was gravure printed on the surface of a sheet of 96g/m² plain white paper in a pattern composed of a number of points, using a cylinder having cells with a diameter of 240 microns. The printing conditions were regulated to obtain the deposit of a layer of the transparentising composition having a thickness in the region of 45 microns.

No suction was applied nor was there any deglossing treatment with a solvent or diluent.

Immediately after the printing the printed surface of the sheet was subjected to irradiation with ultra-violet light from a Philips (Registered Trade Mark) HTQ7 2000 watt high pressure mercury lamp situated 15cm from the surface of the paper without any intervening filter. The radiation continued for twenty seconds. The resulting watermark was composed of a number of translucent spots having a diameter of 520 microns and with the appearance of a traditional watermark. In fact the pattern was visible not only by transmitted light but equally by reflection from the surface of the paper on which the composition was printed.

The watermark pattern became a little fainter but remained perfectly visible after treatment for an hour in a mixture of equal volumes of toluene and methylethylketone brought to boiling point.

Example 2

The process as described in the Example 1 was repeated but during the printing a suction corresponding to the depression of 8 cm of mercury was applied to the opposite face of the paper.

The spots of the resulting watermark pattern had a diameter of 330 micron thus demonstrating the deterioration in the definition of the pattern obtained when suction is not used.

Example 3

The process of example 2 was repeated but a suction corresponding to a depression of 33 cm of mercury was applied. The spots of the resulting watermark pattern has a

diameter of 320 microns.

Example 4

The process was carried out as in Example 2 except that, before the irradiation, a wad of cotton impregnated with trichlorethylene was pressed lightly against the face of the paper on which the composition had been printed.

After the irradiation the translucence of the watermark was no different but one could not observe the pattern by reflection from the surface of the paper.

Example 5

The process of Example 4 was repeated by the polymerisable transparentising composition consisted in this case of 54% by weight of acrylic acid, 45% by weight of an unsaturated polyester, and 1% by weight of naphthalene sulphochloride. The composition has a viscosity of 550cP at 22°C.

The unsaturated polyester was sold under the mark "Setarol (Registered Trade Mark) 3625" by Kunststoffsabrik Synthese N.V. It was solid at ambient temperature. It was derived from isophthalic acid, had a maximum acid index of 27, a viscosity of between 8 and 16 P at 20°C when in 60% solution in toluene, and a specific gravity of 1.15 at 20°C.

The transparentising composition was printed on one surface of paper using the continuous screen printing process.

The paper was subsequently exposed to ultra-violet radiation for fifteen seconds.

The resulting simulated watermark had properties analogous to those described in Example 4. In particular the watermark had a very good resistance to yellowing and in fact its yellowing was no more than that of the base paper after exposure to daylight for two months.

Example 6

The process of example 4 was repeated but as the transparentising composition there was used a mixture of 10% by weight acrylic acid, 79% by weight pentaerythritoltetracrylate, 10% by weight of a polyester resin of low molecular weight and low degree of unsaturation produced by the Mitchell and Smith Company under the mark "Polymaster (Registered Trade Mark) 2460", and 1% by weight of paratoluene sulphonyl chloride. The composition had a viscosity of 550 cP at 22°C.

The composition was printed on paper by continuous screen printing and the paper was subsequently subject to ultra-violet radiation for ten seconds.

The resulting watermark had characteristics similar to those described in Example 4.

Example 7

A transparentising composition was prepared consisting of 45% unsaturated polyester resin sold under the name Alpolit

(Registered Trade Mark) VUP 31181 (Resinous Chemicals Division of Berger Chemicals), 35% Diethylene Glycol Diacrylate, 23% Trimethylol Propane Triacrylate, and 2% of an initiator believed to be an acetophenone derivative sold under the name Trigonal P1 (Registered Trade Mark) by Akzo Chemie U.K. Ltd. This composition was applied by gravure printing to the surface of a white printing paper as previously described (Example 1). The mark was deglossed by applying a thin film or methyl ethyl ketone, and the mark was then cured by exposure to U.V. irradiation for 5 seconds. The resulting mark had characteristics similar to those in Example 4, and was substantially insoluble in a boiling mixture of equal volumes of toluene and methyl ethyl ketone.

Example 8

A transparentising composition was prepared consisting of 45% unsaturated polyester resin (Alpolit (Registered Trade Mark) VUP31181), 35% Diethylene Glycol Diacrylate, 23% Trimethylol Propane Triacrylate, and 2% of initiator consisting of equal parts of a benzoin alkyl ether sold under the name Glocure (Registered Trade Mark) 401 by A.B.M. Chemicals Ltd., and 2-t-butyl anthraquinone. This composition was applied to a white printing paper, and deglossed as described in Example 7, and cured by exposure to U.V. irradiation for 4 seconds. The resulting mark had characteristics similar to that described in Example 7.

Example 9

A transparentising composition was prepared containing 45% unsaturated polyester resin (Setarol (Registered Trade Mark) 3265 supplied by Kunstharos Fabrik Synthese N.V.), 45% styrene, 8% acrylic acid, and 2% naphthalene 2-sulphonyl chloride. Into this composition was dispersed 2% by weight of the composition, of finely ground ferrous ammonium sulphate. The resulting composition was applied to a 96 g/m² plain white document paper by printing from a suitably engraved gravure plate in the form of a geometrical pattern. The resulting watermark was deglossed by applying a thin film of methyl ethyl ketone, and the mark was then cured by exposure to U.V. irradiation for 20 seconds.

When contacted with a solution containing 1% of 2,2' bipyridyl in a mixture of 10% ethanol and 90% water an intense red colouration was produced almost instantly in the area of the mark.

Example 10

A transparentising composition was prepared as in example 9. Into this was thoroughly dispersed 2% by weight of the composition, of finely ground potassium ferrocyanide. The resulting composition was

used to produce a simulated watermark as described in example 9.

When contacted with a solution containing 5% of ferric ammonium sulphate in water, an intense blue colouration was produced almost instantly in the area of the mark.

WHAT WE CLAIM IS:

1. A method of producing a simulated watermark in a paper sheet, wherein the sheet is impregnated in the desired watermark pattern by a transparentising composition which is itself fluent, and which is polymerisable upon being activated by radiation to yield an insoluble resin matrix having a refractive index approximating to that of the paper, and the composition is cured in situ by irradiating the sheet with activating radiation.

2. A method according to claim 1, in which the activating radiation is ultraviolet radiation.

3. A method according to claim 2, in which the polymerisable transparentising composition includes at least one ultraviolet radiation-stimulated polymerisation initiator comprising an aryl sulphonyl chloride, an aromatic carbonyl compound, acetophenone or a derivative of acetophenone, benzophenone or a derivative of benzophenone, anthraquinone or a derivative of anthraquinone, or a derivative of xanthone.

4. A method according to any preceding claim, in which the transparentising composition comprises a polymerisable unsaturated monomer and a polymerisable unsaturated prepolymer and a polymerisation initiator that will be stimulated by the radiation, and the composition includes a polyethylenically unsaturated compound.

5. A method according to claim 4, in which the polymerisable transparentising composition is a solution that includes a polymerisable material as solvent for the composition and that is free of other solvent.

6. A method according to claim 4 or claim 5, in which the composition contains an acrylic, methacrylic, vinyl or allylic monomer.

7. A method according to any one of claims 4 to 6, in which the composition contains an unsaturated polyester of a polyhydric alcohol and a polycarboxylic acid.

8. A method according to claim 7, in which the alcohol is ethylene glycol or propylene glycol and the acid is maleic anhydride or fumaric acid.

9. A method according to any one of claims 4 to 8, in which the composition also includes a polymer which reacts with the monomer and/or prepolymer during the irradiation curing.

10. A method according to any of claims 1 to 4, in which the composition

contains also a solvent.

11. A method according to any one of the preceding claims, in which the paper is impregnated with the polymerisable transparentising composition in the selected area by a printing process.

12. A method according to any one of the preceding claims, in which, before the irradiation, a suction is applied to the face of the paper opposite to that to which the polymerisable transparentising composition is applied.

13. A method according to any one of the preceding claims, in which, the surface of the paper, at least in the area of simulated watermark, after impregnation with the polymerisable transparentising composition but before curing of the composition, is treated with a small quantity of a solvent or diluent for the composition.

14. A method according to claim 13, in which the solvent or diluent is applied in a fine spray or by means of a damping roller or pad.

15. A method according to any one of the preceding claims, in which the simulated watermark is provided with a colour tint by incorporating an appropriate colouring material in the transparentising composition.

16. A method according to claim 15, in which the transparentising composition includes a colour former which only produces a colouration when subjected to an appropriate reaction.

17. A method according to any one of claims 1 to 14, in which the base paper contains a colour forming reagent and the transparentising composition contains an inhibiting agent so that when subjected to

an appropriate security reaction, the mark remains uncoloured, but the surrounding paper becomes coloured.

18. A method according to any one of the preceding claims, in which the paper sheet is a sensitised security paper.

19. A method according to any one of claims 1 to 5, in which the polymerisable transparentising composition comprises an acrylated epoxy resin composition; isocyanate adducts obtained by reacting a hydroxy alkyl acrylate ester with a polymer containing isocyanate groups; or an epoxy oil acrylate.

20. A method according to any of claims 1 to 18, in which the composition comprises a di, tri or polyacrylic ester of diethylene glycol, neopentyl glycol, trimethylol propane or pentaerythritol.

21. A method according to claim 1, substantially as described in any one of the examples.

22. A paper having a simulated watermark produced according to any one of the preceding claims.

23. A chemically watermarked paper comprising a paper sheet having a watermark applied in a pattern, the watermark being of cured, insoluble reaction product having a refractive index approximating to that of the paper and which has been produced by irradiation in situ of a fluent, transparentising polymerisable composition with ultraviolet radiation.

For the Applicants,

GILL, JENNINGS & EVERY,
Chartered Patent Agents,
53 to 64 Chancery Lane,
London WC2A 1HN